# RECOVERY OF NICKEL FROM SIMULATED NICKEL BATH SOLUTIONS ON CARBON MATRICES USING AN ELECTROGENERATIVE PROCESS

By

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ABSTRAK

Penyaduran nikel digunakan dengan meluas dalam bidang perhiasan, kejuruteraan, dan pengelektrobentukan. Cara yang lazim digunakan dalam penyingkiran nikel daripada efluen adalah melalui pemendakan nikel dan bahan logam lain sebagai hidroksida atau sulfida. Reaktor elektrokimia berkelompok yang beroperasi di dalam keadaan elektrogeneratif telah digunakan untuk memulihkan nikel daripada larutan rendaman nikel simulasi. Satu tindak balas kimia yang spontan akan berlaku di dalam reaktor dan pengaliran elektrik dihasilkan. Rekabentuk sel kelompok yang telah diubahsuai digunakan bersama katod tiga dimensi iaitu grafit poros dan karbon kekaca berongga. Sistem elektrogeneratif telah ditunjukkan dan prestasi sistem yang menggunakan bahan katod berkarbon untuk pemulihan nikel telah dinilai. Perubahan pada sistem dengan rendaman larutan nikel yang berlainan telah dikaji dengan merekodkan perubahan pada keupayaan katod serta menganalisakan peratus pemulihan nikel dengan menggunakan spetroskopi penyerapan atom. Mikroskopi elektron pengimbas - spektrometri penyerakan tenaga sinar-X dan analisis pembelauan sinar-X telah digunakan untuk menyiasat struktur dan morfologi enapan nikel. RVC merupakan bahan katod yang baik dengan catatan pemulihan tertinggi iaitu 82.4% nikel yang dipulihkan di dalam operasi selama 8 jam daripada larutan nikel keras. Peratus pemulihan nikel adalah 72.6% selepas 8 jam operasi ke atas larutan nikel hitam menggunakan grafit SG-132 sebagai katod. Morfologi enapan nikel pada permukaan karbon daripada larutan nikel hitam, larutan nikel keras dan larutan bersulfat turut dikaji. Enapan nikel pada katod adalah logam nikel tulen.

**RECOVERY OF NICKEL FROM SIMULATED NICKEL BATH SOLUTIONS ON CARBON MATRICES USING AN ELECTROGENERATIVE PROCESS**

## ABSTRACT

Nickel plating is used extensively for decorative, engineering and electroforming purposes. The most widely used method of removing nickel from effluents is to precipitate nickel and other metals as hydroxides or sulfides. A batch electrochemical reactor operating in an electrogenerative mode was used to recover nickel from simulated nickel bath solutions. A spontaneous chemical reaction will take place in the reactor and generate an external flow of current. In this present work, a batch cell with an improved design using three-dimensional cathodes namely porous graphite and reticulated vitreous carbon (RVC) is used. The electrogenerative system was demonstrated and the performance of the system using carbon cathode materials for nickel recovery was evaluated. The behavior of various nickel baths was studied by recording changes in the cathode potential and evaluating the recovery of nickel from such baths by using atomic absorption spectroscopy. Scanning electron microscopy-energy dispersive X-ray spectroscopy and X-ray diffraction analyses were used to investigate the structure and morphology of the deposited nickel. RVC serves as a superior cathode material having the highest recovery rate with 82.4% of nickel being recovered in 8 h of operation from hard nickel bath solutions. The percentage of nickel recovery is 72.6% after 8 h operation on a black nickel bath using SG-132 as a cathode. The morphology of nickel deposits on carbon surfaces from black nickel bath, hard nickel bath and high sulphate bath solutions was also investigated. Deposits from various bath solutions are pure metallic nickel.

# CHAPTER 1: INTRODUCTION

## 1.1 Nickel

Nickel is a lustrous and silvery-white metal which has a melting point of 1453 $^{o}$C, relatively low thermal and electrical conductivities, high resistance to corrosion and oxidation, excellent strength and toughness at elevated temperatures and is capable of being magnetized. It is very durable as a pure metal and alloys readily with many other metals. It is used in pure or alloy forms in coins, in nickel plating or alloyed with chromium and other metals in the production of stainless and heat-resisting steels. The world nickel demand has increased from 1.009 million tonnes in 1998 to 1.278 million tonnes in 2008. The price of nickel peaked in the late 1980s and in May 2007 and then declined until the end of 2008. By August 2009, the price has again reached USD20000 per tonne (International Nickel Study Group, 2010)

## 1.2 Nickel Plating Baths

Table 1.1 summarizes the chemical composition and operating conditions for various nickel electroplating solutions and mechanical properties of deposits from such baths. Many of these solutions were developed to meet specific engineering requirements but are used to a much lesser extent compared to the more popular bath solutions which are the sulphate bath and nickel sulphamate bath solutions. (Di Bari, 1994).

Table 1.1: Summary of the chemical composition and operating conditions of various nickel electroplating solutions and the mechanical properties for deposits from these solutions.

| **Composition, g/L** | **pH** | **$^{o}$C** | **Current Density, A/dm$^2$** | **Vickers Hardness, 100 g load** |
|---|---|---|---|---|
| *Fluoborate*<br>Nickel fluoborate, 225-300<br>Nickel chloride, 0-15<br>Boric acid, 15-30 | 2.5-4 | 38-70 | 3-30 | 125-300 |
| *Hard Nickel*<br>Nickel sulphate, 180<br>Ammonium sulphate, 25<br>Boric acid, 30 | 5.6–5.9 | 43-60 | 2-10 | 350-500 |
| *All-sulphate*<br>Nickel sulphate, 225-410<br>Boric acid, 30-45 | 1.5-4 | 38-70 | 1-10 | 180-275 |
| *All-chloride*<br>Nickel chloride,225-300<br>Boric acid, 30-45 | 1-4 | 50-70 | 2.5-10 | 150-280 |
| *Sulfamate*<br>Nickel sulphamate, 300-450<br>Nickel chloride, 0-30<br>Boric acid, 30-45 | 3.5-5 | | 0.5-30 | 170-230 |
| *High Sulphate*<br>Nickel sulphate, 75-110<br>Sodium sulphate, 75-100<br>Ammonium sulphate, 35<br>Boric acid,15 | 5.3-5.8 | 20-32 | 0.5-2.5 | |
| *Black nickel*<br>Nickel sulphate, 75<br>Ammonium sulphate, 35 | 5.6 | 24-32 | 0.15 | |

In nickel fluorborate baths, the electrolyte is maintained at a pH of 2.0-3.5 using fluoroboric acid. The metal content is maintained at up to 120 g $L^{-1}$ of nickel, which is much higher than in an all-sulphate bath. Coatings from these baths are usually specified for heavy nickel applications and electroforming. The disadvantages of fluoborate baths are the high cost of chemicals needed and the throwing power is less than that of sulphate solutions (Di Bari, 1994).

Hard nickel was developed especially for engineering applications where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required (without the use of sulphur-containing organic addition agents). Close control of pH, temperature and current density is necessary for this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature. The internal stress is slightly higher than in deposits from all-sulphate solutions.

The most common nickel plating bath used is the all-sulphate bath. Typical compositions and operating conditions are shown in Table 1.1. The large amount of nickel sulphate used provides the necessary concentration of nickel ions. Boric acid is used as a weak buffer to maintain pH. The all-sulphate bath has four major advantages that are: simple and easy to use; easily available in high purity grades and relatively inexpensive; less aggressive to plant equipment than nickel chloride solutions; and deposits plated from these solutions are less brittle and show lower internal stress than those plated from nickel chloride electrolytes (Di Bari, 1994).

The advantages of all-chloride nickel plating solutions include the following: low voltage; good polishing characteristics; heavy coatings can be deposited; low pitting; improved cathode efficiency; and no need to cool the plating solution. However, there are disadvantages such as being highly corrosive; nickel chloride is

sometimes less pure than nickel sulphate; mechanical properties of the deposit are not as good as those from the Watts bath (Di Bari, 1994).

Sulphamate bath solutions are based on nickel salts of sulphamic acid and the pH is adjusted using sulphamic acid, nickel oxide or carbonate. Nickel coatings from these types of bath usually have very low stress values and high elongations. Another advantage is that it is possible to operate the sulphamate bath without difficulties related to anode dissolution at low chloride levels or even without chloride. The principle advantage of this bath is that it can be operated at nickel concentrations of 180-200 g $L^{-1}$. This allows for the use of high current densities without losing the properties of the coating (Di Bari, 1994).

Black nickel plating is lustrous and has a black or dark gray color. Plating is done with little or no agitation. Occasionally it is necessary to remove hydrogen gas (bubbles) from the parts of the surface using wetting agents. The pH of the bath ranges from 5-6, and the temperature varies from ambient to 60 $^{o}$C. Current density remains at approximately 0.5 A $dm^{-2}$.

## 1.3 Industrial Effluents Containing Nickel

Effluents from mining and metallurgical processes often contain metal ions. All effluents must be treated to conform to limits set up by The Environmental Quality Act, 1974.

The Department of Environment reported higher concentrations of heavy metals in the waters off the west coast of Peninsular Malaysia compared to other areas because of the greater extent of land use and industrialization. In 1990, among the rivers that recorded samples exceeding the standard values of 0.02 mg $L^{-1}$ lead were Sg. Perak, Sg. Selangor, Sg. Kelang, Sg. Linggi and Sg. Melaka. Rivers with

zinc levels exceeding 0.4 mg $L^{-1}$ included Sg. Sepang, Sg. Langat and Sg. Kelang. Sg. Bernam, in the west coast of Peninsular Malaysia, recorded copper values higher than the proposed value of 0.012 mg $L^{-1}$. Rivers that recorded values exceeding the proposed value of 0.004 mg Hg $L^{-1}$ included Sg. Muar, Sg. Duyong, Sg. Kurau, Sg. Bernam, Sg. Selangor and Sg. Kelang. Cadmium and arsenic concentrations were negligible in most of the rivers monitored. Almost all the samples collected from the coastal waters of Malaysia contained values of lead, copper and cadmium above the proposed standards of 0.05 mg $L^{-1}$ lead, 0.01 mg $L^{-1}$ copper and 0.005 mg $L^{-1}$ cadmium. The coastal waters of Perak and Penang recorded high levels of cadmium, copper, lead, mercury and nickel. In 1990, around 50 per cent of the 41 samples collected from Perak had values exceeding the proposed standard of 0.005 mg Hg $L^{-1}$. In 1989, more than 80 % of the 42 samples collected from the coastal waters of Perak had values above the proposed standard of 0.01 mg Ni $L^{-1}$. In Penang, all the samples analyzed for nickel exceeded this value (Choo *et al*., 1994).

## 1.4 Environmental Regulations

Many industries produce dangerous substances in their working cycles. The world production of wastes is constantly increasing, especially in the industrialized countries (Veglio *et al.*, 2003). The presence of heavy metals such as copper, nickel, chromium, lead, mercury and cadmium in aquatic environments is known to cause severe damage to aquatic life beside the fact that these metals kill microorganisms during the biological treatment of wastewater with a consequent delay of the process of water purification. Most of the heavy metal salts are soluble in water and form aqueous solutions, and consequently cannot be separated by ordinary physical means of separation. Nickel is one such toxic substance, the fresh acute criterion for nickel is 1400 μg $L^{-1}$ and the chronic criterion is 160 μg $L^{-1}$ (Suter II and Tsao,1996).

Strict environmental regulations are being imposed on the plating industry throughout the world. The major problem facing nickel platters is to prevent nickel and other metallic ions from entering the environment via plant effluents. The most widely used method of removing metals from effluents is to precipitate nickel and other metals as hydroxides or sulfides. The solid waste is then disposed of in landfills. As the number of landfill sites is limited and because disposal of solid waste is expensive and wasteful, the recovery of metal values by applying reverse osmosis, ion exchange, electrowinning and other methods is economically appealing. Nickel producers accept nickel-containing sludge for recycling through smelters or special plants (Di Bari, 1994).

The Environmental Quality Act, 1974 provides the legal basis for environmental management in general and pollution control in particular. The most relevant subsidiary legislation on water pollution control is the Sewage and Industrial Effluents Regulations, 1979 (SIER). According to Malaysia's Environmental Law,

Environmental Quality Act, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000 states that the parameter limits for Standards A (applies to the industrial and development projects which are located in the water catchment area) and B (applies to the general industrial and development projects) for nickel is 0.2 mg $L^{-1}$ and 1.0 mg $L^{-1}$ respectively (Department of Environment, 2007).

The exposure to soluble nickel compounds can occur through inhalation, ingestion, and eye or skin contact. Although nickel compounds are not absorbed in sufficient concentration through the skin to cause systemic toxicity, they are capable of inducing contact dermatitis in sensitive individuals. Nickel is also, relatively, non-toxic by ingestion. Positive findings in many epidemiology studies attest to the potential human carcinogenicity of nickel compounds. The concentrations of nickel should be kept below the permissible exposure limits established by law (Di Bari, 1994).

## 1.5 Treatment Technologies

With large quantities of wastes produced every year, it is of great interest to develop new treatment processes with the aim of reducing the quantity of wastes which will meet the requirements of sustainable development and to recover valuable product (Juttner *et al*., 2000, Veglio *et al.,* 2003).

The conventional techniques used to remove toxic metals from galvanic waste waters is to precipitate using lime such as $Ca(OH)_2$ or NaOH. This has resulted in large volumes of toxic hydroxide sludge, requiring storage and maintenance (Calzado *et al*., 2005).

Electrochemical reduction of nickel has been carried out in a gas diffusion electrode packed bed electrode cell (GBC) from dilute artifical solutions and industrial wastewater (Njau and Janssen, 1995, Njau *et al.,* 1998, Njau *et al.,* 2000, Koene and Janssen, 2001). Nickel ions are reduced in a divided GBC with hydrogen on the hydrophobic side of a gas diffusion electrode using an external current source between the hydrogen gas diffusion electrode and the packed bed electrode. Studies done by Njau, nickel deposition from industrial solution has revealed three types of deposit that can be obtained using electrochemical removal. As reported, dendrite formation on the membrane is a great problem and the deposit growing on the cathode using three-dimensional cathode for nickel deposition gives practically no industrial advantage. The removal of nickel ions from dilute solutions has also been carried out using a hybrid system that combined an ion-exchange column with an electrodialysis cell. In this way, the properties of ion-exchange materials are combined with the advantages of an electrically driven migration process (Spoor *et al*., 2001a, 2001b, 2002a, 2002b, 2002c). Orhan *et al*. (2002) used an electrolytic process for the recovery of nickel from the rinse waters of plating baths in a rotating packed bed. The treatment of rinsing waters from electroless nickel plating containing a few (2-10) mg $L^{-1}$ of nickel with a biologically active moving bed sand filter was carried out by Pümpel *et al*. (2001). The bioslugde containing the biosorbed nickel was separated from the wash water and thickened in bag filters which then has 2% nickel in the dry matter. The nickel has to undergo pyrometallurgical treatment to be returned to the metal cycle.

Many environmental problems can be tackled using electrochemical techniques and cathodic removal of toxic metal ions from aqueous solutions has been carried out using electrochemical technology (Hor and Mohamed, 2003, Lupi and

Pasquali, 2003, Friedrich *et al*., 2004, Hor and Mohamed, 2005). Conventional, two-dimensional electrode cells have severe performance limitations. Porous three-dimensional electrodes can provide a high rate of metal ion removal, even when treating dilute metal ion solutions (Ponce de Leon and Pletcher, 1994, Reade *et al*., 2004a, 2004b). A three-dimensional electrode can be obtained in a number of ways, including a fluidized bed, a packed bed, or the use of porous material, such as copper-plated, reticulated polyurethane and nickel mesh (Friedrich *et al*., 2004). Metals can be deposited on high surface area per unit volume cathodes having a porous, three-dimensional structure and a surface of an inner rotating cathode cylinder such as stainless steel (Walsh, 2001).

Efforts in the development of three-dimensional electrode technology for the removal of metal ions from effluents has led to the appearance on the market of several technologies (Pletcher *et al*., 1991) shown in Figure 1.1 such as the Reno cell, rotating cylinder cells, enhanced flow plate cells, air sparged tank cells and tank cells. Most of these systems are known to operate most satisfactorily when the metal ion concentration is significantly greater than 10 ppm. On the other hand, maximum metal ion levels permitted in discharges are commonly below 1 ppm (Pletcher *et al*., 1991).

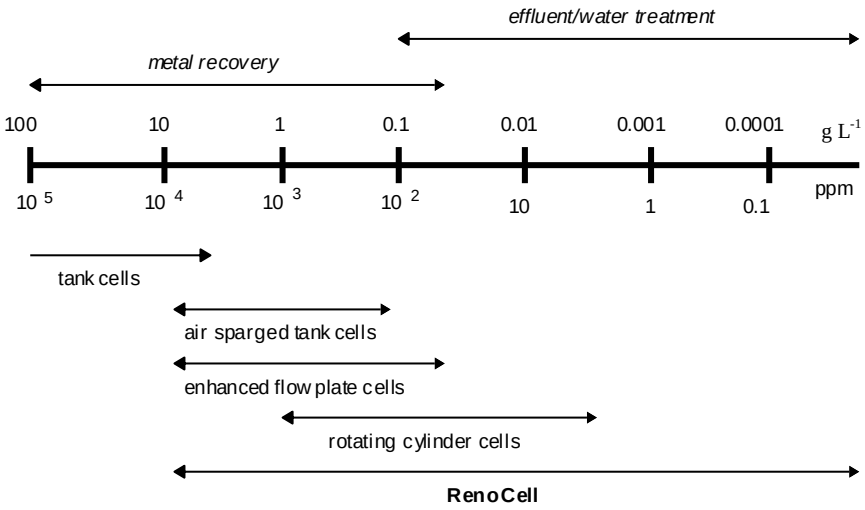


Figure 1.1 - Electrochemical cells for metal recovery - The dependence of cell design on the concentration of metal ions in the feed (Kniazewycz and Lemon (1999)**.**

## 1.6 Objectives of Study

Large quantities of industrial wastewater containing low concentrations of heavy metal ions are produced. The objective of this project is to recover nickel from simulated nickel bath solutions with an electrogenerative process. A spontaneous chemical reaction will take place in the reactor and generate an external flow of current. The reactions in the batch reactor can be represented by the following equations ($E^0$ are standard reduction potentials for half reactions written as reduction) :

| | | | |
|---|---|---|---|
| Anode | : $Zn \rightleftharpoons Zn^{2+} + 2e^-$ | $E^0 = -0.76$ V | (1) |
| Cathode | : $Ni^{2+} + 2e^- \rightleftharpoons Ni$ | $E^0 = -0.25$ V | (2) |
| Overall | : $Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni$ | $E^0 = 0.51$ V | (3) |

There is no requirement for external energy which will reduce the operating costs in effluent treatment. The system will avoid the precipitation process. This is proposed in order to reduce the concentration of the waste material and to recover the valuable metal. The metallic nickel that has been deposited can be reused as anode material or dissolved in acid solution and added to a plating bath. The electrochemical reduction of nickel ions from a dilute solution will be carried out in a batch cell.

A batch electrochemical reactor operating in an electrogenerative mode was used with three-dimensional cathodes namely porous graphite and reticulated vitreous carbon (RVC). Several factors will be investigated such as

(i) type of electrolyte,

(ii) type of anode and cathode used,

(iii) different pH,

(iv) use of membrane in a divided cell and

(v) presence of dissolved oxygen in the catholyte.

The deposited nickel was characterized by means of Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Microanalysis (EDX), X-Ray Diffraction (XRD) and the chemical analyses for concentration of nickel were carried out using Atomic Absorption Spectrometry (AAS).

# CHAPTER 2: EXPERIMENTAL

## 2.1 Galvanic Cell Design

The design of the galvanic batch cell is an improved modification of a cell design by Wan Ngah (1996) which is given in Figure 2.1 where the distance between the electrodes has been minimised. The cell contains two compartments of dimensions 40 mm x 40 mm x 80 mm separated by an anion exchange membrane. The galvanic components were sandwiched together with 8 bolts and nuts. A zinc anode of 99% purity (20 mm x 50 mm) which was polished with sand paper and copper strips (20 mm x 40 mm) used as current collectors were tightly bound together using polytetrafluoroethylene film (PTFE) and placed 5 mm away from the membrane in the anodic compartment. Graphite (SG-132) or reticulated vitreous carbon (RVC 80 ppi) both sized, 20 mm x 50 mm x 10 mm was treated and placed 5 mm away from the membrane in the cathodic compartment. A saturated calomel electrode (SCE) with a Luggin capillary is used as the reference electrode and placed in the cathodic compartment.

## 2.2 Electrode Material

### 2.2.1 Cathode

Two types of porous three-dimensional cathodes were used: porous graphite sheet (SG-132) (The Electrosynthesis Co.) and reticulated vitreous carbon (RVC) 80 pores per inch or ppi (The Electrosynthesis Co.). Both cathodes were sized 20 mm x 50 mm x 10 mm.

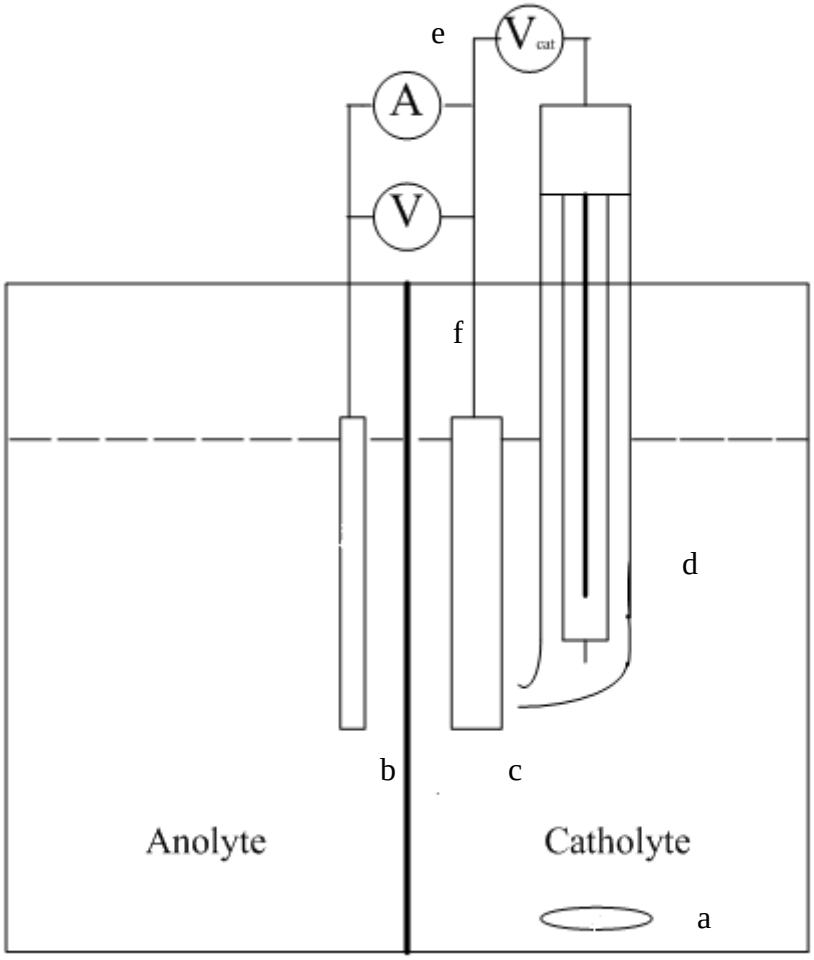


Fig 2.1: Schematic diagram of batch cell showing: (a) magnetic stirrer, (b) zinc plate anode, (c) cathode, (d) SCE, (e) multimeter, (f) anion exchange membrane.

Pretreatment of the porous graphite and RVC are necessary to improve surface wetting characteristics. Initially, the electrodes were rinsed under running tap water and soaked in a beaker containing 95% ethanol : water (v/v) for 4 h. They were then rinsed with sufficient deionized water before being soaked in concentrated sulphuric acid solution for another 4 h. Finally, they were rinsed thoroughly with deionized water and stored in deionized water until ready for use. Used electrodes were stripped of any deposits by soaking in 30% (v/v) nitric acid overnight. After the electrodes were rinsed with deionized water, they will under go pretreatment again before being stored for future use.

### 2.2.2 Anode

A zinc anode with 99% purity (20 mm x 50 mm) was used. Zinc is chosen due to its lower standard reduction potential than nickel. The electrodes were first polished with sand paper and then washed with sufficient deionized water.

## 2.3 Ion Exchange Membranes

A thin sheet or film of ion-exchange material is used to separate ions by allowing the preferential transport of either cations (in the case of a cation-exchange membrane) or anions (in the case of an anion exchange membrane). If the membrane material is made from only ion-exchanging material, it is called a homogeneous ion-exchange membrane. If the ion-exchange material is embedded in an inert binder, it is called a heterogeneous ion-exchange membrane.

In this case, the membrane used is Neosepta AM-1, a heterogeneous anion exchange membrane from Tokuyama Corp. The characteristics of the AM-1 membrane are shown in Table 2.1.

Table 2.1 Characteristics of membrane AM-1

| **Grade** | **Neosepta AM-1** |
|---|---|
| Electric Resistance ($\Omega$ $cm^2$) | 1.5 |
| Water Content ( % wt) | 0.30 |
| Ion Exchange Capacity ( meq $g^{-1}$) | 2.00 |
| Thickness (mm) | 0.16 |
| Burst Strength (kg $cm^{-2}$) | 3.0 – 3.5 |

Source: (Sata, 1992)

The membrane was cut to a size of 80 mm x 90 mm. They were soaked in deionized water prior to any use. In the cell assembly, the membrane is sandwiched between two rubber gaskets to prevent electrolyte leakage. After each experiment, the cell compartments were filled with deionized water to keep the ion exchange membrane moist.

## 2.4 Multimeters

The output current and potential of the system were measured with a Fluke 77 Series II Multimeter and Sanwa digital multimeter.

## 2.5 Resistance Box

The Resistance Box 1051, supplied by Time Electronic Ltd, has variable resistance values ranging from 0.00 Ω to 999,999.99 Ω.

## 2.6 Electrolytes

All solutions were prepared from analytical grade chemicals using deionized water. Catholyte solutions which contained 1000 ppm Ni were prepared to simulate various nickel plating baths namely all sulphate bath, black nickel bath and hard nickel bath. The types catholyte solutions used in this work are given in Table 2.2.

### 2.6.1 Catholyte

#### 2.6.1 (a) All sulphate bath

A typical composition of an all sulphate bath for nickel plating consists of $NiSO_4.6H_2O$ and $H_3BO_3$ (Brillas *et al.*, 1999). Boric acid is normally used to act as a buffer.

Table 2.2 Types of catholyte solutions used.

| Simulated spent plating bath | Chemicals | Source of Chemicals | Composition |
|---|---|---|---|
| Black nickel | $NiSO_4.6H_2O$ | R&M Chemicals | 8.95 g $L^{-1}$ |
| | $(NH_4)_2SO_4$ | SYSTEM ChemAR @ | 33.03 g $L^{-1}$ |
| Hard nickel | $NiSO_4.6H_2O$ | R&M Chemicals | 8.95 g $L^{-1}$ |
| | $(NH_4)_2SO_4$ | SYSTEM ChemAR @ | 33.03 g $L^{-1}$ |
| | $H_3BO_3$ | R&M Chemicals | 37.10 g $L^{-1}$ |
| All sulphate | $NiSO_4.6H_2O$ | R&M Chemicals | 8.95 g $L^{-1}$ |
| | $H_3BO_3$ | R&M Chemicals | 37.10 g $L^{-1}$ |

### 2.6.1 (b) Black nickel bath

Black nickel baths are commercially used, but are limited in its applications. The process was developed for decorative reasons - color matching and blending. There are sulphate and chloride black nickel plating baths (Di Bari, 1994). In these studies, a sulphate black nickel bath consisting of $NiSO_4.6H_2O$ and $(NH_4)_2SO_4$ was used.

### 2.6.1 (c) Hard nickel bath

Hard nickel baths were developed especially for engineering applications where controlled hardness, improved abrasion resistance, greater tensile strength and good ductility are required. For optimum results, the ammonium ion concentration should be maintained at 8 g $L^{-1}$.

## 2.7 Anolyte

A fixed concentration of 1.00 M of sodium sulphate was used throughout this work. The use of $Na_2SO_4$ as an anolyte produced the highest current efficiency and nickel flux (Spoor *et al*., 2001b).

## 2.8 pH Control

Cathodic nickel reduction is thermodynamically possible within the pH range of 4.9-8.3 (Orhan, 2002). The pH was adjusted manually using sulphuric acid and ammonia sulphate ( Amblard *et al*.,1982).

## 2.9 Sampling

Sampling of the catholyte is done by pipeting 0.4 µL using a micropipette (Model PipetPlus Rainin Instruments Co. Inc.) into a 100 mL volumetric flask. The sample is diluted to 100 mL with a dilution factor of 250. A volume of 0.4 µL of deionized water is then added into the catholyte.

## 2.10 Ni Standard Solutions

A 1000 ppm standard nickel solution (Merck) which has a composition of $Ni(SO_4)_2$ in 0.5 mol $L^{-1}$ $HNO_3$ was used. 10 mL of nickel standard solution was pipetted into a 100 mL volumetric flask. The solution is topped up to 100 mL with deionized water producing a 100 ppm Ni(II). 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm Ni standard solutions were prepared from the 100 ppm Ni standard in 100 mL volumetric flacks.

## 2.11 Determination of Nickel Concentration

An atomic absorption spectrophotometer (AAS) model AAnalyst 200 (Perkin Elmer) is used to determine the concentration of nickel(II) in the catholyte.

## 2.12 Mechanical Convection

A stirring hotplate (Favorit) is used to enhance mechanical convection in the catholyte solutions with a scale of 4. In previous studies utilizing a rotating zinc electrode and rotating packed cell, the rotation speed was reported to play an effect in Ni cementation (Makhloufi *et al*., 1998; Orhan *et al*., 2002).

## 2.13 Experimental Approach

Seven aspects to be studied have been identified that is the effect of cathode potential, ion exchange membrane, cathode material, anode material, surface area, catholyte composition, pH, dissolved oxygen and the morphology of nickel deposits on carbon surface. As a test of reproducibility, a particular experimental run was performed three times.

### 2.13.1 The effect of cathode potential

The system was initially loaded with maximum resistance which was gradually decreased until it was short-circuited. In all experiments, 3 minutes were required to reach a steady state after each change of cathodic potential. Three replicate polarization curves were recorded to ensure reproducibility. After the initial open circuit cell voltage was read, the resistance was gradually decreased by adjusting the variable resistance of a decade resistance box. At the end of the predetermined interval, cell potential, cathode potential and current readings were recorded. Measurements for two different cathodic polarization curves were taken with the parameters as shown in Table 2.3.

### 2.13.2 The effect of ion exchange membrane

Two different ion exchange membranes, a cation exchange membrane and an anion exchange membrane were used. The study on the effect of the type ion exchange membrane was carried out with the parameters as shown in Table 2.4.

Table 2.3 Experimental parameters to study the effect of cathode potential

| **Parameters** | |
|---|---|
| Mechanical Convection | Speed / scale 4 |
| Anode | 99 % zinc |
| Cathode | 1) Graphite SG-132<br>2) RVC-80 ppi |
| Anolyte | 1.0 M $Na_2SO_4$ |
| Catholyte | 1) Black nickel bath<br>2) Hard nickel bath<br>3) All sulphate bath |
| Membrane | Neosepta AM-1 |
| pH | 5-8 |
| Temperature | 27$^{o}$C |
| Purging | No |

Table 2.4 Experimental parameters to study the effect of ion exchange membrane

| **Parameters** | |
|---|---|
| Mechanical Convection | Speed / scale 4 |
| Anode | 99 % zinc |
| Cathode | RVC-80 |
| Anolyte | 1.0 M $Na_2SO_4$ |
| Catholyte | Black nickel bath |
| Membrane | Neosepta AM-1<br>CM-1 |
| pH | 5-7 |
| Temperature | $27^oC$ |
| Purging | No |

### 2.13.3 The effect of cathode material

The study on the effect of cathode material was carried out with the parameters as shown in Table 2.5.

### 2.13.4 The effect of anode material

Four different metal electrodes were studied (iron bar, aluminum bar, galvanized zinc plate and 99% purity zinc foil). The study on the effect of anode material was carried out with the parameters as shown in Table 2.6.

### 2.13.5 The effect of cathode thickness

Deposition of nickel on porous graphite SG-132 of different thickness was studied with the parameters as shown in Table 2.7.

### 2.13.6 The effect of catholyte composition

The catholyte solutions used were black nickel, hard nickel and all sulphate solutions. These bath solutions are widely used throughout the world. The study on the effect of catholyte compositions was carried out with the parameters as shown in Table 2.8.

### 2.13.7 The effect of pH

Nickel deposition was highly affected by the changes in pH (Njau and Janssen, 1995). The pH ranges between pH 5 to 7 and without pH control were studied in this work. The study on the effect of pH was carried out with the parameters as shown in Table 2.9.

Table 2.5 Experimental parameters to study the effect of cathode material

| **Parameters** | |
|---|---|
| Mechanical Convection | Speed / scale 4 |
| Anode | 99 % zinc |
| Cathode | 1) Stainless steel<br>2) Copper plate<br>3) Graphite SG-132<br>4) RVC-80 |
| Anolyte | 1.0 M $Na_2SO_4$ |
| Catholyte | Black nickel bath |
| Membrane | Neosepta AM-1 |
| pH | 5-7 |
| Temperature | $27^oC$ |
| Purging | No |